



# Photocatalytic hydrogen peroxide production by anthraquinone-augmented polymeric carbon nitride

Hyoung-il Kim<sup>a,c</sup>, Yeoseon Choi<sup>b</sup>, Shu Hu<sup>c</sup>, Wonyong Choi<sup>b</sup>, Jae-Hong Kim<sup>c,\*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Yonsei University, Seoul, 03722, Republic of Korea

<sup>b</sup> Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 37673, Republic of Korea

<sup>c</sup> Department of Chemical and Environmental Engineering, School of Engineering and Applied Science, Yale University, New Haven, CT, 06511, United States

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## ABSTRACT

We describe the exploitation of the selective catalytic property of anthraquinone (AQ) for solar photocatalytic synthesis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as a green, sustainable alternative to organic-solvent-based and energy-intensive industry-benchmark processes that also rely on AQ catalysis. We accomplished this by anchoring AQ onto polymeric carbon nitride (C<sub>3</sub>N<sub>4</sub>), a metal-free visible light photocatalyst (band gap energy = 2.7 eV), that has been previously demonstrated for selective H<sub>2</sub>O<sub>2</sub> synthesis. A net H<sub>2</sub>O<sub>2</sub> production rate of 361 μmol g<sup>-1</sup> h<sup>-1</sup> and an apparent quantum yield (AQY) of 19.5% at 380 nm excitation were achieved using AQ-augmented C<sub>3</sub>N<sub>4</sub> under simulated 1-sun illumination in the presence of an organic electron donor (2-propanol); these results were 4.4-fold and 8.3-fold higher than those reported for bare C<sub>3</sub>N<sub>4</sub>, respectively. A suite of experimental analyses confirmed the unique roles of AQ co-catalysis in (i) capturing electrons from the conduction band of C<sub>3</sub>N<sub>4</sub>, thereby reducing futile exciton recombination, which is otherwise prevalent in bare C<sub>3</sub>N<sub>4</sub>; (ii) effectively mediating electron transfer to drive hydrogenation reaction to form anthrahydroquinone (AQH<sub>2</sub>) from AQ; and (iii) catalyzing oxygen reduction to H<sub>2</sub>O<sub>2</sub> through the dehydrogenation of AQH<sub>2</sub> back to AQ, resulting in the facile and selective formation of H<sub>2</sub>O<sub>2</sub>. In addition, the reduced decomposition of produced H<sub>2</sub>O<sub>2</sub> by the C<sub>3</sub>N<sub>4</sub>/AQ composite photocatalysts, when compared to bare C<sub>3</sub>N<sub>4</sub> or C<sub>3</sub>N<sub>4</sub> composited with common metallic co-catalysts such as Pt and Ag, was found to contribute to the significant enhancement in H<sub>2</sub>O<sub>2</sub> production through the oxidation of both organic and water.

## 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a widely used commodity chemical with an estimated global gross production of 3 million metric tons per year [1]. It is an environmentally friendly and easy-to-handle oxidant, since it generates only water and oxygen after its use. Due to a relatively high oxidation potential ( $E_0 = 1.763$  V vs. NHE at pH 0), H<sub>2</sub>O<sub>2</sub> can oxidize a variety of organic and inorganic substrates through facile liquid- or vapor-phase reactions [2]. These unique properties allow H<sub>2</sub>O<sub>2</sub> to function in a broad range of industrial and commercial applications in the chemical production, medical practice, and environmental remediation. In particular, a large quantity of H<sub>2</sub>O<sub>2</sub> is used in the advanced oxidation process in water and wastewater treatment as a precursor for producing hydroxyl radicals via UV irradiation and catalyst (e.g., reduced Fe and Cu) activation [3,4].

H<sub>2</sub>O<sub>2</sub> is also considered an alternative liquid fuel with higher energy density than compressed H<sub>2</sub> gas (200 psi). Concentrated H<sub>2</sub>O<sub>2</sub> has been used as a liquid fuel for propulsion and actuation [5]. Chemical energy

stored in H<sub>2</sub>O<sub>2</sub> can be converted to electricity on demand via a H<sub>2</sub>O<sub>2</sub> fuel cell [6,7], or to H<sub>2</sub> by applying a small voltage (~0.6 V). The exhaust from either process does not produce greenhouse gases, but only oxygen and water. Up to a 0.8 V open-circuit voltage has been reported with H<sub>2</sub>O<sub>2</sub> fuel cells, which rivals state-of-the-art H<sub>2</sub> fuel cells [8]. Despite established industrial use as well as growing interest in both environment and energy sectors, the current H<sub>2</sub>O<sub>2</sub> production technology is energy- and chemical-intensive and far from being carbon neutral within its life cycle, significantly limiting its sustainable growth.

Solar-driven photocatalytic production of H<sub>2</sub>O<sub>2</sub> has been emerging as an environmentally friendly and sustainable alternative because its production requires only sunlight, water, and air [9,10]. At present, the most common H<sub>2</sub>O<sub>2</sub> production process is based on the anthraquinone (AQ) method, also referred to as the Riedl–Pfleiderer process, which involves hydrogenation and auto-oxidation as the first two steps (Fig. S1) [11]. In the first step, hydrogenation, 2-alkyl-anthraquinone (R-AQ) is hydrogenated catalytically to alkyl-anthrahydroquinone (R-AQH<sub>2</sub>) by reacting with H<sub>2</sub> on a catalyst surface in a solvent (e.g., triethyl

\* Corresponding author.

E-mail address: [jaehong.kim@yale.edu](mailto:jaehong.kim@yale.edu) (J.-H. Kim).

phosphate and trimethyl benzene). In the second step, oxidation, the hydrogenated R-AQH<sub>2</sub> is oxidized by oxygen (typically by oxygen in air) to revert to R-AQ with the concurrent H<sub>2</sub>O<sub>2</sub> production. Although this industry standard process achieves relatively high H<sub>2</sub>O<sub>2</sub> yields due to AQ's exceptional selectivity toward H<sub>2</sub>O<sub>2</sub>-evolving reactions, it requires costly hydrogen gas and noble metals, toxic organic solvents, and a large energy input to provide the necessary high temperature [12]. Alternative processes which can directly synthesize H<sub>2</sub>O<sub>2</sub> on metal catalysts (e.g., Pd or Pd/Au alloys) from the hydrogen and oxygen gas have been explored, but these processes require a large amount of energy and also face the risk of explosion of the H<sub>2</sub>/O<sub>2</sub> gaseous mixture [13,14].

Polymeric carbon nitride (C<sub>3</sub>N<sub>4</sub>) has been considered one of the most suitable photocatalysts to achieve this goal for several reasons. First, C<sub>3</sub>N<sub>4</sub> is metal free and exhibits superior stability and excellent optical absorption of visible light. It can be readily synthesized by the heat-induced polymerization of various precursors such as melamine and therefore is relatively inexpensive [15]. Second, unlike metal oxide semiconductors [16], C<sub>3</sub>N<sub>4</sub> not only catalyzes water-splitting (1.8 vs. RHE and −0.9 vs. RHE for the valence band and conduction band, respectively) [17] but also exhibits selectivity towards H<sub>2</sub>O<sub>2</sub> production through the sequential formation of a superoxo radical and 1,4-endoperoxide species [18,19]. Third, C<sub>3</sub>N<sub>4</sub> exhibits relatively narrow bandgap energy (2.6–2.7 eV) compared to most UV absorbers like TiO<sub>2</sub>, allowing it to utilize the visible portion of the solar spectrum. Note that co-catalysts are commonly used with small-bandgap photocatalysts (< 2.7 eV) to improve rates of charge transfer and multi-electron catalysis and to prevent rapid recombination of excited charges or excitons by charge separation; noble metals and carbon materials (e.g., Au [20], Au–Ag [21], Au–Pd [22], graphene [9], graphene oxide (GO) [23], reduced GO (rGO) [24]) are benchmark co-catalysts due to their ability to withdraw electrons from conduction bands and transfer them to electron acceptors. However, these co-catalysts either decompose H<sub>2</sub>O<sub>2</sub> or exhibit poor selectivity towards the selective 2-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>.

We present here a new approach that leverages the exceptional activity and selectivity of AQ chemistry for reductive H<sub>2</sub>O<sub>2</sub> synthesis using C<sub>3</sub>N<sub>4</sub> particles as a visible light absorber. Different from the industrial process, the molecular AQ catalysts are augmented onto heterogeneous surfaces of C<sub>3</sub>N<sub>4</sub> particles such that AQ chemistry can be solar-driven (Scheme 1). In this mechanism, AQ withdraws electrons from the C<sub>3</sub>N<sub>4</sub> conduction band such that (1) AQ functions as a co-catalyst to minimize charge recombination and ultimately enhance the quantum yield, overcoming the limitation of small-bandgap photocatalysts [25]; and (2) AQ transfers electrons to initiate the electron-coupled hydrogenation reaction (AQ to AQH<sub>2</sub>) with a low-lying reduction potential (0.1 V vs. NHE) [26]. Subsequently, H<sub>2</sub>O<sub>2</sub> is synthesized as oxygen is reduced through the dehydrogenation reaction of AQH<sub>2</sub> to AQ. C<sub>3</sub>N<sub>4</sub> is particularly instrumental for this composite material approach since N sites of C<sub>3</sub>N<sub>4</sub> offer a molecular handle for grafting AQ molecules. We successfully synthesized AQ-augmented C<sub>3</sub>N<sub>4</sub> (in this study termed C<sub>3</sub>N<sub>4</sub>/AQ) and performed various photo (electro)chemical characterizations to demonstrate highly efficient photocatalytic H<sub>2</sub>O<sub>2</sub> generation at a production rate of 361 μmol g<sup>−1</sup> h<sup>−1</sup>. This rate is a 4.4-fold higher value than that of bare C<sub>3</sub>N<sub>4</sub> (82.3 μmol g<sup>−1</sup> h<sup>−1</sup>) under simulated solar illumination.

## 2. Experiments

### 2.1. Synthesis of C<sub>3</sub>N<sub>4</sub> photocatalysts

A batch of C<sub>3</sub>N<sub>4</sub> was prepared by heating melamine (99%, Aldrich) at 550 °C, which was reached at a ramp rate of 2.5 °C min<sup>−1</sup>, for 3 h in an alumina boat crucible covered with a lid. After cooling to RT, the collected sample was suspended in DI water. Unreacted melamine was removed by filtering the suspension (Supor®, 0.45 μm, Pall

Corporation) and washed with DI water several times. The purified C<sub>3</sub>N<sub>4</sub> was dried at 70 °C overnight for further use. Melem was prepared by the same process except that the temperature was raised to 425 °C at 2.5 °C min<sup>−1</sup> and kept for 6 h.

### 2.2. Synthesis of AQ-augmented C<sub>3</sub>N<sub>4</sub> composite

AQ-augmented C<sub>3</sub>N<sub>4</sub> was prepared through the catalyst-free direct coupling method [27]. As-prepared C<sub>3</sub>N<sub>4</sub> (0.2 g) was suspended in 18 mL of acetonitrile (99.8%, Aldrich) and a varying amount (1–20 wt% with respect to C<sub>3</sub>N<sub>4</sub>) of anthraquinone-2-carboxylic acid (AQ-COOH, 98%, Aldrich) was added to the suspension. The suspension was sonicated for 30 min and stirred for 12 h at 50 °C. After cooling down to RT, the suspension was filtered (Supor®, 0.45 μm, Pall Corporation), washed several times with DI water and ethanol to remove remaining AQ-COOH, and dried overnight at 70 °C. Composites of C<sub>3</sub>N<sub>4</sub> with AQ derivatives with different functional groups (2-aminoanthraquinone, Aldrich), sodium anthraquinone-2-sulfonate (≥98%, Aldrich), and 2-(hydroxymethyl)anthraquinone (97%, Aldrich)) were also prepared following the same synthetic procedure. AQ-augmented melem (melem/AQ) was prepared by the same procedure as for C<sub>3</sub>N<sub>4</sub>/AQ, but substituting melem for C<sub>3</sub>N<sub>4</sub>.

### 2.3. Synthesis of C<sub>3</sub>N<sub>4</sub> composite with metal co-catalysts

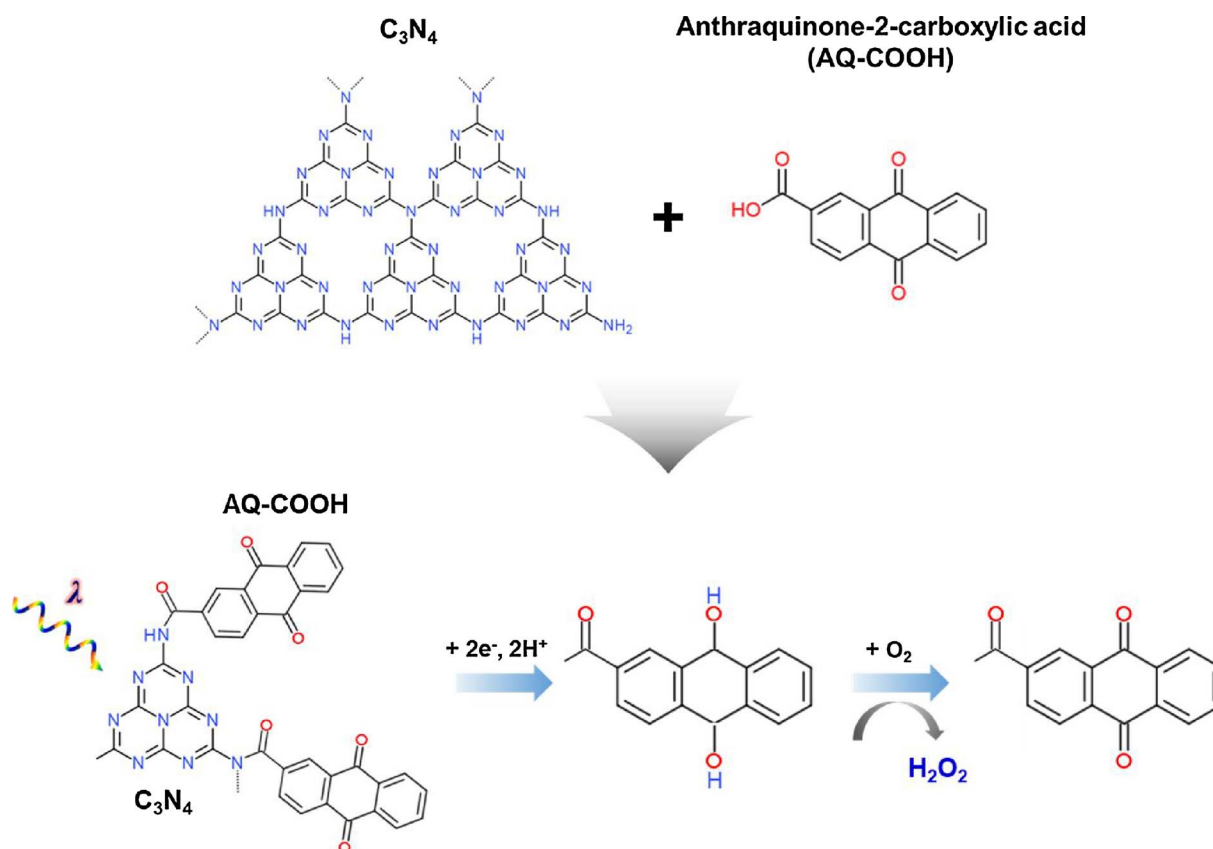
Composites of C<sub>3</sub>N<sub>4</sub> with various noble metal co-catalysts were prepared via a well-established photo-deposition method [28] using hydrogen tetrachloroaurate trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O, ≥99.9%, Aldrich), chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Aldrich), and silver nitrate (AgNO<sub>3</sub>, ≥99.0%, Aldrich) as metal precursors. An aqueous suspension containing C<sub>3</sub>N<sub>4</sub>, one of these metal precursors, and an electron donor (10 vol% methanol) was irradiated by a white LED (100 W) for 4 h for photo-deposition of the respective metal co-catalysts.

### 2.4. Synthesis of C<sub>3</sub>N<sub>4</sub> composite with carbon co-catalysts

C<sub>60</sub> (1 wt%)-loaded C<sub>3</sub>N<sub>4</sub> was prepared following the previously established procedure with a slight modification [29]. The melamine (1 g) and C<sub>60</sub> (0.5 or 10 mg, SES Research, 99.9%) were first grounded together using mortar and pestle for 10 min. The mixture was then placed in an alumina boat crucible covered with a lid and heated at 550 °C for 3 h following the same procedure for bare C<sub>3</sub>N<sub>4</sub> synthesis. C<sub>3</sub>N<sub>4</sub> was also loaded with GO and rGO (10 wt%), prepared by the modified Hummers method and by further reducing GO with hydrazine [30], respectively. The GO or rGO suspension (2.0 mg/mL) was added to the aqueous suspension of C<sub>3</sub>N<sub>4</sub> that had been ultrasonicated for 3 h to exfoliate C<sub>3</sub>N<sub>4</sub>. This mixture was further ultrasonicated for 3 h, vigorously stirred for additional 6 h, washed with DI water, and dried at 80 °C overnight.

### 2.5. Characterization

The crystalline phases of C<sub>3</sub>N<sub>4</sub> and modified C<sub>3</sub>N<sub>4</sub> samples were analyzed using a powder X-ray diffraction (XRD) with Cu Kα radiation (MAC Science, M18XHF). Diffuse reflectance spectra (DRS) were obtained using a Varian Cary 3 spectrophotometer equipped with an integrating sphere, and their band gaps were estimated using Tauc's plot. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Theta Probe AR-XPS System (Thermo Fisher Scientific) with a monochromatic Al Kα source (1486.6 eV). Fourier transform infrared (FT-IR) spectra were obtained using a Thermo Scientific Nicolet 6700 FT-IR spectrometer.



**Scheme 1.** Schematic illustration of the process to couple  $C_3N_4$  with AQ(–COOH) and the photocatalytic hydrogen peroxide generation process by AQ(–COOH)-coupled  $C_3N_4$  under solar light irradiation.

## 2.6. Photocatalytic $H_2O_2$ production

Photocatalytic  $H_2O_2$  production experiments were carried out by irradiating simulated solar light ( $AM\ 1.5$ ,  $100\ mW\ cm^{-2}$ ) from a 150-W Xenon Arc lamp to the aqueous suspension of  $0.5\ g/L$  of differently modified  $C_3N_4$  containing 2-propanol (10 vol%) as an electron donor. The suspension was continuously purged with  $O_2$  for 20 min before and during illumination. The incident light intensity was determined using a Newport calibrated Si solar cell. The concentration of produced  $H_2O_2$  was colorimetrically determined using titanium(IV) sulfate (30% Solution, Fisher Scientific) that forms pertitanic acid ( $H_2TiO_4$ ) upon reaction with  $H_2O_2$  [31]. Briefly, a sample aliquot was collected from the reaction suspension using a syringe, filtered through a syringe filter ( $0.45\ \mu m$  PTFE, Pall), and mixed with a titanium (IV) sulfate solution (0.64%, diluted by sulfuric acid). The absorbance at  $\lambda_{max}$  (405 nm) of pertitanic acid in the mixture was monitored using a UV/visible spectrophotometer ( $\epsilon = 730\ M^{-1}\ cm^{-1}$ ) [31]. A DPD (N,N diethyl-1,4 phenylenediamine sulfate) colorimetric method ( $\epsilon = 21,000\ M^{-1}\ cm^{-1}$ ) [10,32] was also used for the samples with relatively low  $H_2O_2$  concentration ( $100 \leq \mu M$ ). Apparent quantum efficiency (AQY) was characterized by illuminating the suspension of  $C_3N_4$  and  $C_3N_4/AQ$  in the presence of 2-propanol electron donor with monochromated light ( $\lambda = 380, 400, 420, 450$ , and  $480\ nm$ ) through bandpass filters (Thorlabs).

## 2.7. Photoelectrochemical characterization

Photoelectrochemical (PEC) characterizations were conducted using a conventional three-electrode potentiostat setup connected to a Gamry potentiostat (Reference 600). The PEC reactor consisted of two coiled Pt wires and a saturated Ag/AgCl/KCl (sat) electrode as working, counter, and reference electrodes, respectively. The photocurrent derived from photo-generated charge carriers on photocatalysts was collected on a Pt

working electrode (at  $1.1\ V$  vs. RHE ( $0.8\ V$  vs. Ag/AgCl)) through  $Fe^{3+}/Fe^{2+}$  electron shuttles ( $0.2\ mM$ ) in the photocatalyst suspension ( $0.5\ g\ L^{-1}$ ,  $[NaClO_4] = 0.1\ M$ ,  $pH_i = 1.8$ ) under simulated solar illumination ( $AM\ 1.5$ ,  $100\ mW\ cm^{-2}$ ). Electrochemical (EC) characterization was performed in a PEC reactor that consisted of a glassy carbon electrode (GCE, CH Instruments (CHI104),  $3.0\ mm$  diameter), a coiled Pt wire, and a saturated Ag/AgCl/KCl (sat) electrode as working, counter, and reference electrodes, respectively. The GCE was loaded with photocatalysts fabricated by first mixing catalysts (10 mg) with Nafion resin binder ( $60\ \mu L$ , 5 wt% Alfa Aesar Nafion perfluorinated resin in a mixture of water and 1-propanol), further dissolving the mixture in 2-propanol ( $800\ \mu L$ ), depositing the final mixture onto the electrode and drying at RT, and further drying at  $105\ ^\circ C$  overnight. Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were obtained at a scan rate of  $50\ mV\ s^{-1}$  over a range of potentials (from  $-1.2$  to  $+1.0$  vs. Ag/AgCl for CV and from  $-1.1$  to  $+0.6\ V$  vs. Ag/AgCl for LSV). Electrochemical impedance spectroscopy (EIS) analysis was performed at a DC voltage of  $-0.5\ V$  vs. Ag/AgCl, an AC voltage amplitude of  $50\ mV$ , and a frequency ranging from  $500\ mHz$  to  $100\ kHz$ .

## 3. Results and discussion

### 3.1. Characterization of $C_3N_4/AQ$

A successful synthesis of  $C_3N_4$  from melamine was first confirmed by XRD, UV-vis, and FT-IR absorption spectral analyses (Fig. 1). When the reaction synthesis reached around  $425\ ^\circ C$ , we observed the formation of a condensed carbon nitride compound, melem ( $C_6N_7(NH_2)_3$ ), as indicated by a typical monoclinic unit cell XRD diffraction pattern (Fig. 1a; see Fig. S2 for the reaction scheme) [33]. Further reaction at a higher temperature ( $550\ ^\circ C$ ) leads to additional condensation and

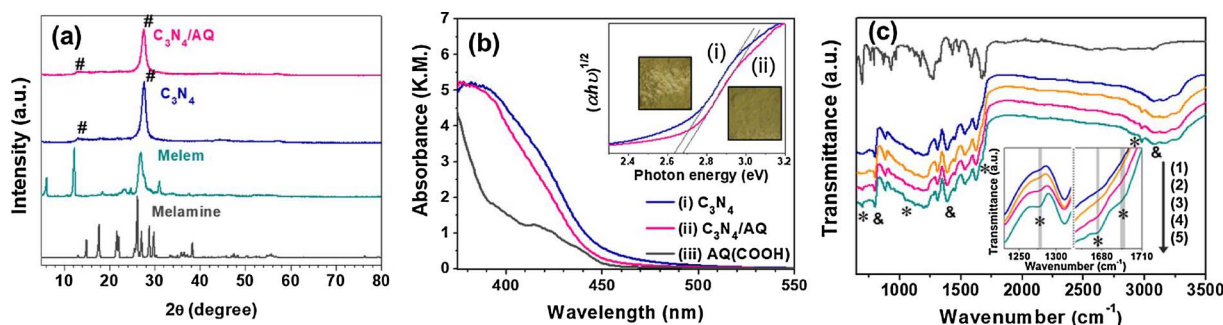


Fig. 1. (a) XRD spectra of melamine, melem, C<sub>3</sub>N<sub>4</sub>, and C<sub>3</sub>N<sub>4</sub>/AQ(-COOH). '#' in (a) represents two main diffraction peaks (13.0° (100) and 27.4° (002)) of C<sub>3</sub>N<sub>4</sub> -[34]. Absorption intensities in (b) were expressed in the Kubelka–Munk unit (KM =  $(1 - R^2)/2R$ ). The inset in (b) shows the photographs and the estimated band gaps (using Tauc's plot) of C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>4</sub>/AQ(-COOH), assuming indirect transitions. (c) FT-IR spectra of (1) AQ(-COOH), (2) C<sub>3</sub>N<sub>4</sub>, (3) C<sub>3</sub>N<sub>4</sub>/AQ (5 wt%), (4) C<sub>3</sub>N<sub>4</sub>/AQ (10 wt%), and (5) C<sub>3</sub>N<sub>4</sub>/AQ (20 wt%). The inset in (c) shows the magnified FT-IR spectra in the range between 1230 and 1320 cm<sup>-1</sup> and between 1660 and 1710 cm<sup>-1</sup>, respectively. Notations '\*' and '&' in (c) represent main absorption peaks of C<sub>3</sub>N<sub>4</sub> and AQ induced absorption peaks on C<sub>3</sub>N<sub>4</sub>/AQ, respectively.

formation of C<sub>3</sub>N<sub>4</sub>, one of the most stable allotropes of carbon nitride, that consists of tri-s-triazine (C<sub>6</sub>N<sub>7</sub>) units as evidenced by the XRD peak at 27.4° (002) [34]. The band-edge wavelength of the C<sub>3</sub>N<sub>4</sub> was at 470 nm (Fig. 1b), which corresponds to band gap energy ( $E_{BG}$ ) of ca. 2.64 eV according to Tauc's plots (Fig. 1b inset,  $(\alpha h\nu)^{1/2} \propto (h\nu - E_g)$ ) and confirms C<sub>3</sub>N<sub>4</sub>'s visible light absorption capability [25,35]. The FT-IR spectrum of C<sub>3</sub>N<sub>4</sub> (Fig. 1c) was characterized by the triazine unit's breathing mode peak at 798 cm<sup>-1</sup> as well as a skeletal stretching mode peak of C–N at 1250–1420 cm<sup>-1</sup> and C≡N bonds at 1550–1630 cm<sup>-1</sup>, respectively [36,37]. Broad absorption peaks at 3050–3400 cm<sup>-1</sup> belong to edge amino groups (–NH/NH<sub>2</sub>) [37,38].

The crystal structure of C<sub>3</sub>N<sub>4</sub> was not affected by AQ coupling, as evidenced by the XRD spectrum where only slight broadening of main diffraction peaks (13.0° (100) and 27.4° (002)) was observed (Fig. 1a). The band-edge wavelength appeared slightly blue-shifted by 10 nm, and  $E_{BG}$  marginally increased to 2.68 eV from 2.64 eV after coupling with AQ (Fig. 1b). This minor change is attributed to AQ(–COOH)'s lower absorbance and narrower absorption band than C<sub>3</sub>N<sub>4</sub>, as the spectrum reflects the mixed absorption of C<sub>3</sub>N<sub>4</sub> and AQ(–COOH). The result suggests that there is no direct optical transition between C<sub>3</sub>N<sub>4</sub> and AQ. In contrast, we observed a gradual change in FT-IR spectra with increasing AQ(–COOH) contents (Fig. 1c). Peaks centered at 698 cm<sup>-1</sup> and 2974 cm<sup>-1</sup>, corresponding to C–H bending and stretching vibrations from AQ, respectively, confirm AQ coupling [39,40]. The increase in absorption at 1278 cm<sup>-1</sup> and 1676 cm<sup>-1</sup>, corresponding to C–N stretching and carbonyl C=O stretching vibrations, respectively, indicates the amide bond formation [41,42]. However, the separate absorption band of amide N–H vibrations at 3320 cm<sup>-1</sup> was not observed, due to the overlap with the broad absorption of uncondensed amine groups (3050–3400 cm<sup>-1</sup>) [38,42,43].

XPS analysis provided clearer evidence of the covalent bonding of AQ–COOH to C<sub>3</sub>N<sub>4</sub>. In the C1s spectrum, C<sub>3</sub>N<sub>4</sub> showed a weak peak at a binding energy of 284.8 eV and a prominent peak at 288.2 eV; these peaks are assigned to the C–C bonding of surface adventitious carbon/defect-derived sp<sup>2</sup>-carbon and the N–C≡N bond in the triazine units, respectively (Fig. 2a) [44]. When coupled with AQ, a strong aromatic C–C bonding peak at 284.8 eV, originating from AQ, emerged from the background of adventitious carbon [45]. In the O1s spectra, AQ coupling resulted in the decrease and shift (toward higher energy) of the COOH peak at 533.2 eV and > C=O peak at 531.4 eV, concurrent with formation of the amide bond (O=C–N, at 532.4 eV) from the reaction between –COOH in AQ and –NH<sub>2</sub> in C<sub>3</sub>N<sub>4</sub> (Fig. 2b) [45,46]. The weak peak at 532.2 eV on C<sub>3</sub>N<sub>4</sub> is attributed to adsorbed CO<sub>2</sub> or H<sub>2</sub>O on the surface [47]. In N1s spectra, both C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>4</sub>/AQ displayed a similar shape composed of three major peaks at ca. 398.6, 399.8, and 400.8 eV; the peak shape corresponds to sp<sup>2</sup>-hybridized aromatic N in the form of C=N–C, the ternary N–(C)<sub>3</sub> groups, and the sp<sup>3</sup>-hybridized amino functional groups, respectively (Fig. 2c) [48]. However,

the peak for amide that forms as a result of the reaction between AQ and C<sub>3</sub>N<sub>4</sub> was indistinguishable from the peak for amino functional groups of C<sub>3</sub>N<sub>4</sub>. Collectively, these results indicate that AQ molecules were successfully augmented to C<sub>3</sub>N<sub>4</sub> without significant structural changes by the simple heat-induced hybridization procedure.

### 3.2. Photocatalytic H<sub>2</sub>O<sub>2</sub> production by C<sub>3</sub>N<sub>4</sub>/AQ

Results shown in Fig. 3a and summarized in Table 1 suggest that C<sub>3</sub>N<sub>4</sub> photocatalytically produces H<sub>2</sub>O<sub>2</sub> under solar-simulated light illumination, and the rate of production is faster when C<sub>3</sub>N<sub>4</sub> is coupled with AQ compared to other commonly used co-catalysts (refer to Figs. S3 and S4 for their properties). The noble metals such as Ag, Au, and Pt deposited onto the photocatalyst function as co-catalysts, promoting interfacial electron transfer from the conduction band of C<sub>3</sub>N<sub>4</sub> to the electron acceptor and thereby reducing futile exciton recombination [49,50]. Accordingly, H<sub>2</sub>O<sub>2</sub> production increased by approximately 60% and 80% (from 82.3 to 132 and 147 μmol g<sup>-1</sup> h<sup>-1</sup>) by Ag and Au loading, respectively. In contrast, carbon-based co-catalysts (C<sub>60</sub>, GO, and rGO) were detrimental to H<sub>2</sub>O<sub>2</sub> production (H<sub>2</sub>O<sub>2</sub> production rate reduced by 32%, 24%, and 10% with C<sub>60</sub> (1 wt%), GO (10 wt%), and rGO (10 wt%), respectively), presumably due to accelerated single-electron transfer to oxygen leading to the formation of superoxide radical anion, instead of forming H<sub>2</sub>O<sub>2</sub> through two-electron transfer [51,52].

When C<sub>3</sub>N<sub>4</sub> was coupled with AQ (10 wt%), the H<sub>2</sub>O<sub>2</sub> production rate was significantly increased to a rate 4.4 times higher than that of bare C<sub>3</sub>N<sub>4</sub>, from 82.3 to 361 μmol g<sup>-1</sup> h<sup>-1</sup>. The kinetic enhancement was dependent on the amount of AQ loaded onto C<sub>3</sub>N<sub>4</sub>; the maximum rate was achieved at 10 wt% (Fig. S5). The decrease in the H<sub>2</sub>O<sub>2</sub> production rate at higher AQ loading is likely to have resulted from the light shielding, as the absorption of AQ overlaps with C<sub>3</sub>N<sub>4</sub> in the UV region. Similar observations have been reported for other carbon-based co-catalysts such as carbon nanotubes, GO, and rGO [53,54]. These results suggest AQ plays a critical role in significantly enhancing production of H<sub>2</sub>O<sub>2</sub> via photocatalysis. We found that the H<sub>2</sub>O<sub>2</sub> production rate was also enhanced when AQ was physisorbed onto C<sub>3</sub>N<sub>4</sub>; a strong physisorption is expected through  $\pi$ - $\pi$  interaction between basal planes of AQ and C<sub>3</sub>N<sub>4</sub>, similar to the interaction between AQ and graphene [55]. AQ derivatives with different functional groups, such as –OH, –SO<sub>3</sub><sup>-</sup>, –NH<sub>2</sub> instead of –COOH or without a functional group (bare AQ), all enhanced H<sub>2</sub>O<sub>2</sub> production but to a much lesser extent than when AQ(–COOH) was grafted to C<sub>3</sub>N<sub>4</sub> via amide bonding (Fig. 3b). Although  $\pi$ - $\pi$  interaction between C<sub>3</sub>N<sub>4</sub> and AQ(–COOH) cannot be ruled out, this chemical grafting in C<sub>3</sub>N<sub>4</sub>/AQ(–COOH) appeared necessary not only to bind AQ securely onto the photocatalyst to prevent co-catalyst detachment over time but also to more effectively utilize AQ chemistry.



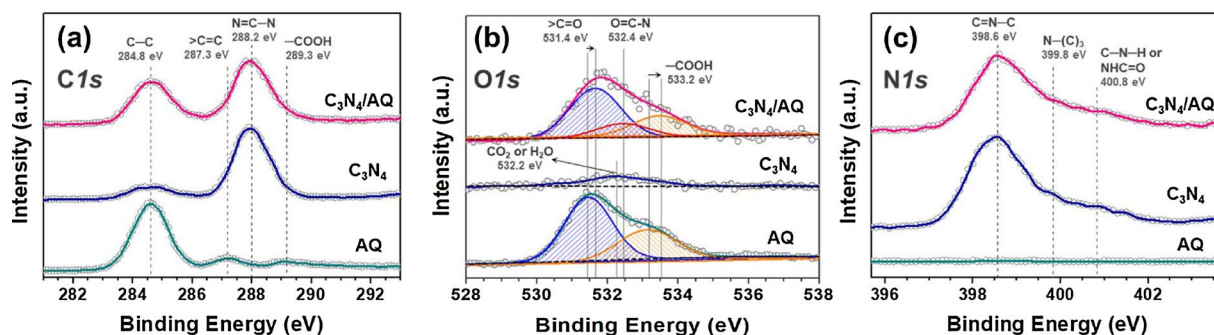


Fig. 2. XPS spectra of (a) C1s, (b) O1s, and (c) N1s on AQ(-COOH), C<sub>3</sub>N<sub>4</sub>, and C<sub>3</sub>N<sub>4</sub>/AQ(-COOH) (10 wt%).

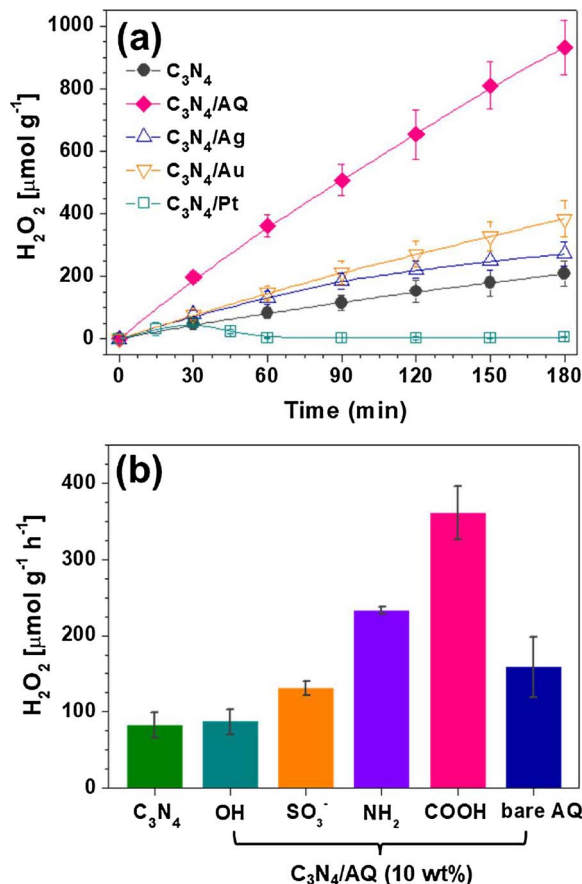


Fig. 3. (a) Time-dependent profiles of H<sub>2</sub>O<sub>2</sub> production by C<sub>3</sub>N<sub>4</sub>, C<sub>3</sub>N<sub>4</sub>/AQ(-COOH), and C<sub>3</sub>N<sub>4</sub>/Ag, Au, Pt) metals (1 wt%) with 2-propanol as the electron donor. (b) H<sub>2</sub>O<sub>2</sub> production as a function of anchoring groups of AQ molecules on C<sub>3</sub>N<sub>4</sub>/AQ (after 1 h reaction). The experimental conditions were as follows: [catalyst] = 0.5 g L<sup>-1</sup>, [2-propanol]<sub>0</sub> = 10 vol%, pH<sub>i</sub> = not adjusted, 100 mW cm<sup>-2</sup> (AM 1.5), and O<sub>2</sub>-saturated.

### 3.3. Mechanism of AQ co-catalysis

The occurrence of C<sub>3</sub>N<sub>4</sub>-driven AQ chemistry in the C<sub>3</sub>N<sub>4</sub>/AQ composite is manifested by the fact that a saturated AQ solution (30 μM) under otherwise identical conditions (e.g., [2-propanol]<sub>0</sub> = 10 vol%, O<sub>2</sub>-saturated, 100 mW cm<sup>-2</sup> irradiation by solar simulator) produced a negligible amount of H<sub>2</sub>O<sub>2</sub> (Fig. S6). A photocatalytic H<sub>2</sub>O<sub>2</sub> generation by AQ alone under UV irradiation is, in fact, possible through the electron transfer mediation by excited triplet-state of AQ to oxygen [56], but such generation is much less efficient compared to the proton-coupled electron transfer (PCET) that occurs on C<sub>3</sub>N<sub>4</sub>/AQ [57]. Negligible production of H<sub>2</sub>O<sub>2</sub> on C<sub>3</sub>N<sub>4</sub>/AQ in the absence of O<sub>2</sub> (under N<sub>2</sub>-saturated condition; Fig. S7b) also supports the finding that AQ functions as a catalyst, not as a reactant. Accordingly, repeated use of C<sub>3</sub>N<sub>4</sub>/AQ resulted in a negligible

Table 1  
Photocatalytic production of H<sub>2</sub>O<sub>2</sub> with various modified g-C<sub>3</sub>N<sub>4</sub>.

Samples	Produced H <sub>2</sub> O <sub>2</sub> <sup>a</sup> (μmol g <sup>-1</sup> h <sup>-1</sup> )	k <sub>f</sub> <sup>b</sup> (μmol g <sup>-1</sup> min <sup>-1</sup> )	k <sub>d</sub> <sup>c</sup> (× 10 <sup>4</sup> ) min <sup>-1</sup> )
g-C <sub>3</sub> N <sub>4</sub>	82.3 ± 16.5	1.18 ± 0.04	3.89 ± 0.08
g-C <sub>3</sub> N <sub>4</sub> /AQ-COOH	361 ± 35.4	5.22 ± 0.13	1.83 ± 0.12
g-C <sub>3</sub> N <sub>4</sub> /AQ-OH	86.9 ± 16.6	1.33 ± 0.05	3.12 ± 0.13
g-C <sub>3</sub> N <sub>4</sub> /AQ-SO <sub>3</sub> <sup>-</sup>	131 ± 9.43	2.33 ± 0.07	5.79 ± 0.37
g-C <sub>3</sub> N <sub>4</sub> /AQ-NH <sub>2</sub>	233 ± 4.24	3.63 ± 0.11	2.34 ± 0.15
g-C <sub>3</sub> N <sub>4</sub> /AQ	158 ± 39.6	2.62 ± 0.02	3.34 ± 0.12
g-C <sub>3</sub> N <sub>4</sub> /Pt (1 wt%)	103 ± 10.4	2.46 ± 0.05	252 ± 10.5
g-C <sub>3</sub> N <sub>4</sub> /Ag (1 wt%)	132 ± 19.8	1.64 ± 0.13	10.4 ± 0.16
g-C <sub>3</sub> N <sub>4</sub> /Au (1 wt%)	147 ± 22.2	2.22 ± 0.04	5.06 ± 0.19
g-C <sub>3</sub> N <sub>4</sub> /C60 (0.05 wt%)	63.2 ± 6.54	1.04 ± 0.05	3.21 ± 0.41
g-C <sub>3</sub> N <sub>4</sub> /C60 (1 wt%)	56.0 ± 13.2	0.98 ± 0.01	2.73 ± 0.02
g-C <sub>3</sub> N <sub>4</sub> /GO (10 wt%)	62.3 ± 13.6	1.09 ± 0.05	3.78 ± 0.09
g-C <sub>3</sub> N <sub>4</sub> /rGO (10 wt%)	74.3 ± 17.4	1.18 ± 0.04	3.28 ± 0.14
Melem	74.0 ± 3.78	1.03 ± 0.04	5.66 ± 0.59
Melem/AQ-COOH	315 ± 29.2	4.49 ± 0.13	2.89 ± 0.50

<sup>a</sup> Production rate was estimated by fitting the data (for initial 1 h except C<sub>3</sub>N<sub>4</sub>/Pt (1 wt %)).

<sup>b</sup> k<sub>f</sub> (μmol g<sup>-1</sup> min<sup>-1</sup>).

<sup>c</sup> k<sub>d</sub> ((× 10<sup>4</sup>) min<sup>-1</sup>) were evaluated by assuming the zero-order and first-order kinetics, respectively, through the eqn. of  $\left[ \text{H}_2\text{O}_2 \right] = \frac{k_f}{k_d} \{1 - \exp(-k_d t)\}$ . All values of C<sub>3</sub>N<sub>4</sub>/Pt (1 wt%) were evaluated with H<sub>2</sub>O<sub>2</sub> production rate for the initial 30 min.

change in photocatalytic properties (Fig. S8). We also observed that the effect of oxygen concentration on H<sub>2</sub>O<sub>2</sub> production was less profound for C<sub>3</sub>N<sub>4</sub>/AQ than bare C<sub>3</sub>N<sub>4</sub> (i.e., 16% reduction with C<sub>3</sub>N<sub>4</sub>/AQ compared to 30% reduction with bare C<sub>3</sub>N<sub>4</sub> when the suspension was air-saturated instead of O<sub>2</sub>-saturated), suggesting improved oxygen reduction ability through AQ co-catalysis (Fig. S7a and b). Collectively, these results indicate that the main role of AQ in C<sub>3</sub>N<sub>4</sub>/AQ is co-catalysis leading to accelerated H<sub>2</sub>O<sub>2</sub> production from photo-excited C<sub>3</sub>N<sub>4</sub>.

The enhanced H<sub>2</sub>O<sub>2</sub> production by AQ resulted not only from increased H<sub>2</sub>O<sub>2</sub> formation but also from reduced H<sub>2</sub>O<sub>2</sub> decomposition that occurs through both reductive and oxidative pathways [9]. We separately evaluated the formation (k<sub>f</sub>, μmol g<sup>-1</sup> min<sup>-1</sup>) and decomposition (k<sub>d</sub>, min<sup>-1</sup>) rate constants of H<sub>2</sub>O<sub>2</sub> using the following equation [58,59]:

$$\left[ \text{H}_2\text{O}_2 \right] = \frac{k_f}{k_d} \{1 - \exp(-k_d t)\} \quad (1)$$

Values of k<sub>f</sub> and k<sub>d</sub> obtained by fitting the data in Fig. 3a (photocatalytic H<sub>2</sub>O<sub>2</sub> production) and Fig. 4a (decomposition of H<sub>2</sub>O<sub>2</sub> externally added to the catalyst suspension) to Eq. (1) are summarized in Fig. 4b and Table 1. All C<sub>3</sub>N<sub>4</sub> modified with noble metals exhibited the increased k<sub>f</sub> values up to 2.1 times (2.46 μmol g<sup>-1</sup> min<sup>-1</sup> for C<sub>3</sub>N<sub>4</sub>/Pt) compared to that of bare C<sub>3</sub>N<sub>4</sub> (1.18 μmol g<sup>-1</sup> min<sup>-1</sup>). But at the same time, k<sub>d</sub> values also increased, from 1.3 to 65 times (0.0252 min<sup>-1</sup> for C<sub>3</sub>N<sub>4</sub>/Pt) compared to that of bare C<sub>3</sub>N<sub>4</sub> (0.0004 min<sup>-1</sup>).

Significant decomposition of H<sub>2</sub>O<sub>2</sub> by Pt explains why Pt co-catalyst was not at all effective in enhancing H<sub>2</sub>O<sub>2</sub> production. In the case of

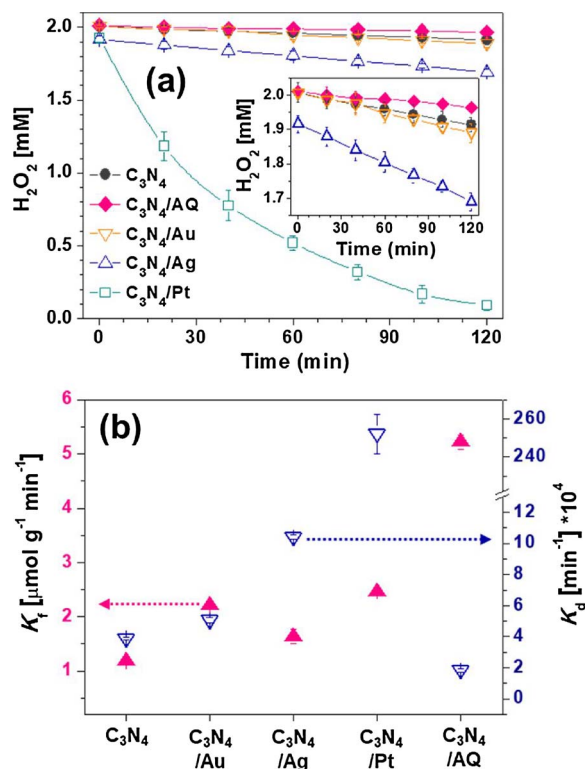


Fig. 4. (a) Time-dependent profiles of photocatalytic decomposition of  $\text{H}_2\text{O}_2$  ( $C_0 = 2 \text{ mM}$ ) by  $\text{C}_3\text{N}_4$ ,  $\text{C}_3\text{N}_4/\text{AQ}(-\text{COOH})$  (10 wt%), and  $\text{C}_3\text{N}_4/(\text{Ag}, \text{Au}, \text{Pt})$  metals (1 wt%). The inset shows the magnified time-dependent profiles of photocatalytic decomposition of  $\text{H}_2\text{O}_2$  ( $C_0 = 2 \text{ mM}$ ) by  $\text{C}_3\text{N}_4$ ,  $\text{C}_3\text{N}_4/\text{AQ}(-\text{COOH})$  (10 wt%), and  $\text{C}_3\text{N}_4/(\text{Ag}, \text{Au})$  metals (1 wt%). (b) Formation rate constants ( $k_f$ , filled symbols) and decomposition rate constants ( $k_d$ , open symbols) for  $\text{H}_2\text{O}_2$ . The experimental conditions were as follows: [catalyst] =  $0.5 \text{ g L}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 2 \text{ mM}$ ,  $\text{pH}_i$  = not adjusted,  $100 \text{ mW cm}^{-2}$  (AM 1.5), and  $\text{O}_2$ -saturated.

$\text{C}_3\text{N}_4/\text{AQ}$ , the  $k_f$  value was the greatest at  $5.22 \pm 0.13 \mu\text{mol g}^{-1} \text{ min}^{-1}$ , and the  $k_d$  value was the smallest at  $0.0002 \text{ min}^{-1}$ , accounting for the highest overall efficiency for  $\text{H}_2\text{O}_2$  production. The effective co-catalysis by AQ was also found by selective  $\text{O}_2$  reduction (leading to  $\text{H}_2\text{O}_2$  formation) instead of  $\text{O}_2$  reduction to water or  $\text{H}^+$  to  $\text{H}_2$  formation, especially when compared to noble metal co-catalysts. The reduction potential for the formation of  $\text{H}_2\text{O}_2$  ( $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$ ,  $E^0 = 0.695 \text{ V}$ ) occurs with a greater thermodynamic driving force than that of  $\text{H}_2$  formation ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ,  $E^0 = 0 \text{ V}$ ) [60]. Since the photocatalytic  $\text{H}_2\text{O}_2$  formation can also be initiated by one-electron transfer reactions ( $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{\cdot-}$ ,  $E^0 = -0.33 \text{ V}$ ;  $\text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{HO}_2^{\cdot}$ ,  $E^0 = -0.046 \text{ V}$ ) [60], both the  $\text{H}_2\text{O}_2$  and  $\text{H}_2$  formation occur competitively in the  $\text{C}_3\text{N}_4$  photocatalytic system. We observed that, under simulated solar irradiation, noble metal-loaded  $\text{C}_3\text{N}_4$  produced a significant amount of  $\text{H}_2$ , for example, at a rate of  $92.9 \pm 4.6 \mu\text{mol g}^{-1} \text{ h}^{-1}$  for  $\text{C}_3\text{N}_4/\text{Pt}$  and  $81.9 \pm 3.4 \mu\text{mol g}^{-1} \text{ h}^{-1}$  for  $\text{C}_3\text{N}_4/\text{Au}$ , while bare  $\text{C}_3\text{N}_4$  and  $\text{C}_3\text{N}_4/\text{AQ}$  produced a negligible amount of  $\text{H}_2$  (Fig. S9). This selectivity toward oxygen reduction through PCET explains the overall high efficiency of  $\text{C}_3\text{N}_4/\text{AQ}$  in  $\text{H}_2\text{O}_2$  production.

In the absence of an organic electron donor (i.e., isopropanol), the co-catalytic activity of AQ was more clearly observed where water was used as an electron donor ( $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$ ) (Fig. S7 a and b).  $\text{C}_3\text{N}_4$  showed a negligible  $\text{H}_2\text{O}_2$  production in the absence of an organic electron donor. A small amount of  $\text{H}_2\text{O}_2$  was produced at an early stage, but it quickly disappeared due to the decomposition of  $\text{H}_2\text{O}_2$  by  $\text{C}_3\text{N}_4$ . In contrast,  $\text{C}_3\text{N}_4/\text{AQ}$  was able to produce  $\text{H}_2\text{O}_2$  continuously during the 3 h reaction (ca.  $110 \mu\text{mol g}^{-1}$ ). Long-term tests more obviously demonstrated the superior  $\text{H}_2\text{O}_2$  production by  $\text{C}_3\text{N}_4/\text{AQ}$  using water as the electron donor (Fig. S7c). These results collectively support the

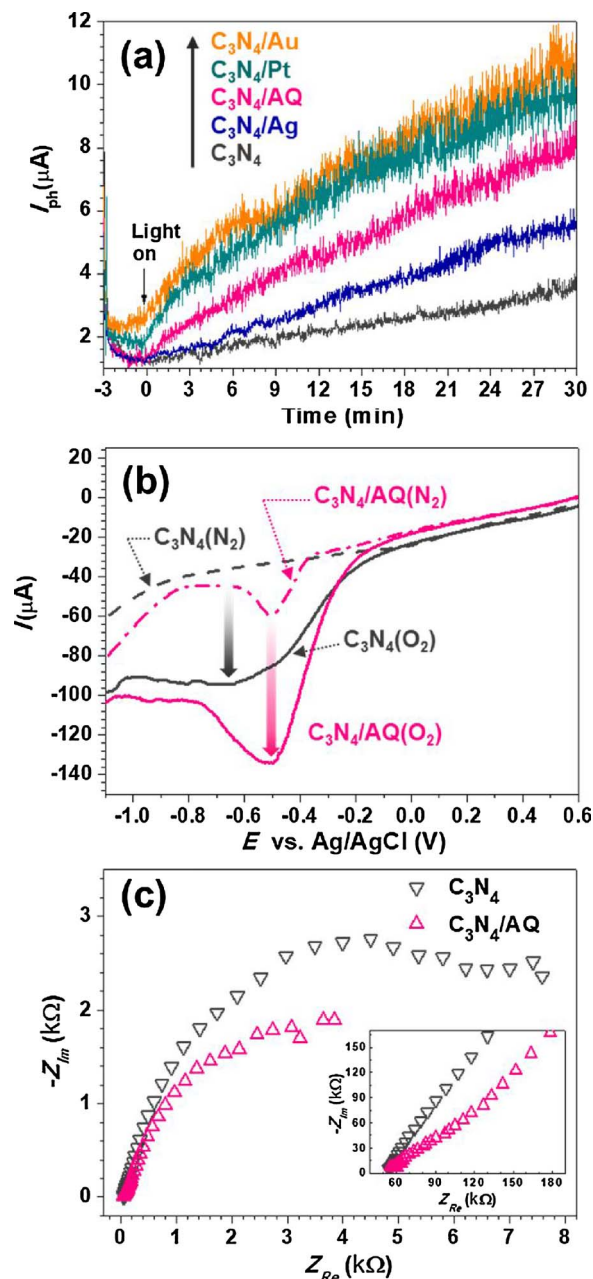


Fig. 5. (a) Time-profiles of  $\text{Fe}^{3+}$ -mediated photocurrent collected on a Pt electrode in the aqueous suspension of  $\text{C}_3\text{N}_4$ ,  $\text{C}_3\text{N}_4/\text{AQ}(-\text{COOH})$  (10 wt%), and  $\text{C}_3\text{N}_4/(\text{Ag}, \text{Au}, \text{Pt})$  metals (1 wt%). The experimental conditions were as follows: [catalyst] =  $0.5 \text{ g L}^{-1}$ ,  $[\text{Fe}^{3+}] = 2.0 \text{ mM}$ ,  $[\text{NaClO}_4] = 0.1 \text{ M}$ ,  $\text{pH}_i = 1.8$ ,  $100 \text{ mW cm}^{-2}$  (AM 1.5), Pt electrode held at  $+0.8 \text{ V}$  (vs. Ag/AgCl), and under  $\text{N}_2$ -purging. (b) LSV curves of  $\text{C}_3\text{N}_4$  and  $\text{C}_3\text{N}_4/\text{AQ}(-\text{COOH})$  (10 wt%) electrodes in  $0.5 \text{ M}$  ( $\text{pH} = 7.0$ ) phosphate buffer solution at a scan rate of  $50 \text{ mV s}^{-1}$  under  $\text{N}_2$ - or  $\text{O}_2$ -purging (without light). (c) Nyquist plots of  $\text{C}_3\text{N}_4$  and  $\text{C}_3\text{N}_4/\text{AQ}(-\text{COOH})$  (10 wt%) electrodes were obtained in the range from  $0.5 \text{ Hz}$  to  $100 \text{ kHz}$  at a representative potential of  $-0.5 \text{ V}$  (vs. Ag/AgCl) under  $\text{O}_2$ -saturated condition, in  $0.5 \text{ M}$  ( $\text{pH} = 7.0$ ) phosphate buffer solution (without light). The inset in (c) shows magnified Nyquist plots at the higher frequency range.

conclusion that the incorporation of AQ plays an essential role in  $\text{H}_2\text{O}_2$  production by accelerating formation kinetics and decelerating decomposition kinetics for  $\text{H}_2\text{O}_2$ .

### 3.4. Photoelectrochemical and electrochemical analyses

We were able to further verify the role of AQ as an electron-withdrawing co-catalyst by measuring a photo-generated current, collected

by the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox shuttle, in a  $\text{C}_3\text{N}_4/\text{AQ}$  suspension under simulated solar irradiation (Fig. 5a) [61]. Compared to bare  $\text{C}_3\text{N}_4$ , the  $\text{C}_3\text{N}_4/\text{AQ}$  exhibited significantly increased photocurrent during light irradiation, which is comparable to those of noble metal-loaded  $\text{C}_3\text{N}_4$  composites. The photocurrent generation during the 30 min reaction ( $I_{\text{ph}}$  at 30 min –  $I_{\text{ph}}$  at 0 min) was  $8.21 \mu\text{A}$  for  $\text{C}_3\text{N}_4/\text{Au}$ ,  $7.94 \mu\text{A}$  for  $\text{C}_3\text{N}_4/\text{Pt}$ ,  $6.82 \mu\text{A}$  for  $\text{C}_3\text{N}_4/\text{AQ}$ ,  $4.28 \mu\text{A}$  for  $\text{C}_3\text{N}_4/\text{Ag}$ , and  $2.29 \mu\text{A}$  for bare  $\text{C}_3\text{N}_4$ , respectively. The Pt wire working electrode was poised at 1.1 V vs. RHE (0.8 V vs.  $\text{Ag}/\text{AgCl}$ ), oxidizing  $\text{Fe}^{2+}$  back to  $\text{Fe}^{3+}$  at an effective anodic current. The relatively sluggish photocurrent generation on  $\text{C}_3\text{N}_4/\text{Ag}$  is due to the slow interfacial electron transfer that occurred on Ag rather than other noble metals [62]. The back reaction of  $\text{C}_3\text{N}_4$  absorbers oxidizing  $\text{Fe}^{2+}$  back to  $\text{Fe}^{3+}$  may occur, reducing the effective anodic currents on an equal basis. The result indicates that AQ functions to separate charges of  $\text{C}_3\text{N}_4$  and transfer electrons to the  $\text{Fe}^{3+}$  redox shuttles in a way similar to how noble metal co-catalysts function.

The charge separated by AQ further contributes to oxygen reduction, as further verified by electrochemical potential sweep measurements performed using photocatalyst-loaded GCE under  $\text{N}_2$  and  $\text{O}_2$  saturated conditions. The CV curve of  $\text{C}_3\text{N}_4$  in Fig. S10a displayed a rectangular shape (the electrical double-layer capacitance) without any peaks under  $\text{N}_2$  saturated condition, whereas a pair of redox peaks was observed at around  $-0.46 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  ( $-0.51 \text{ V}_{\text{Ag}/\text{AgCl}}$  for the cathodic peak and  $-0.42 \text{ V}_{\text{Ag}/\text{AgCl}}$  for the anodic peak) on  $\text{C}_3\text{N}_4/\text{AQ}$  (Fig. S10b). These redox peaks correspond to the aforementioned hydrogenation (AQ to  $\text{AQH}_2$ ) and dehydrogenation ( $\text{AQH}_2$  to AQ) reactions [26] in Scheme 1. In LSV (Fig. 5b), a large increase in the oxygen reduction current along with a reduction peak potential (shifted from  $-0.66 \text{ V}_{\text{Ag}/\text{AgCl}}$  for  $\text{C}_3\text{N}_4$  to  $-0.50 \text{ V}_{\text{Ag}/\text{AgCl}}$  for  $\text{C}_3\text{N}_4/\text{AQ}$ ) under an  $\text{O}_2$  saturated condition with  $\text{C}_3\text{N}_4/\text{AQ}$  also indicates that AQ facilitates the oxygen reduction by utilizing AQ chemistry. It is noteworthy that  $\text{C}_3\text{N}_4/\text{AQ}$  exhibited even greater oxygen reduction activity than  $\text{C}_3\text{N}_4/\text{Au}$ , the noble metal with the highest  $\text{H}_2\text{O}_2$  production potential, with respect to both the oxygen reduction current and the reduction peak potential (Fig. S10c).

The results of EIS analyses, shown as Nyquist plots in Fig. 5c and bode plots in Fig. S11, consistently point toward the occurrence of AQ chemistry in Scheme 1 in our system. The  $\text{C}_3\text{N}_4$  electrode resulted in a large hemisphere in the Nyquist plot that fit well to a single-capacitance Randles circuitry. In contrast, the  $\text{C}_3\text{N}_4/\text{AQ}$  electrode exhibited two incomplete hemispheres with data fitting to a double-capacitance Randles circuitry. The result is likely to have come from the involvement of two-step reactions: the first capacitive arc from the reaction leading to the formation of  $\text{AQH}_2$  by the hydrogenation of AQ, and the second capacitive arc from the reaction  $\text{AQH}_2$  with  $\text{O}_2$  to form  $\text{H}_2\text{O}_2$ . In addition, the total resistance of  $\text{C}_3\text{N}_4/\text{AQ}$ , the sum of  $R_{\text{CT1}}$  (for  $\text{AQH}_2$  formation) and  $R_{\text{CT2}}$  (for  $\text{H}_2\text{O}_2$  production), was much smaller than that ( $R_{\text{CT}(\text{total})}$ ) of  $\text{C}_3\text{N}_4$  (Fig. S11 table). The PEC/EC results above confirm the involvement of AQ chemistry for  $\text{H}_2\text{O}_2$  production when composited with  $\text{C}_3\text{N}_4$ .

### 3.5. $\text{H}_2\text{O}_2$ Production by melem/AQ composite

We further confirmed the role of AQ in photocatalytic  $\text{H}_2\text{O}_2$  production by attaching AQ on melem, a subunit of  $\text{C}_3\text{N}_4$ . Melem's photocatalytic property is analogous to that of  $\text{C}_3\text{N}_4$  but with greater bandgap energy [33,63]. The ending amine groups on melem can also be combined with the AQ-COOH in the same way as with  $\text{C}_3\text{N}_4$  and AQ (-COOH). The results from FT-IR and XPS showed that attaching AQ to melem results in characteristic changes similar to those resulting from attaching AQ to  $\text{C}_3\text{N}_4$  (Fig. S12).

The trend with melem was similar to that with  $\text{C}_3\text{N}_4$ : incorporating AQ onto melem increased  $\text{H}_2\text{O}_2$  production (Fig. 6a) due to 4-times higher formation rate constant (from  $1.03 \mu\text{mol g}^{-1} \text{min}^{-1}$  to  $4.49 \mu\text{mol g}^{-1} \text{min}^{-1}$ ) and a 2-times smaller decomposition rate

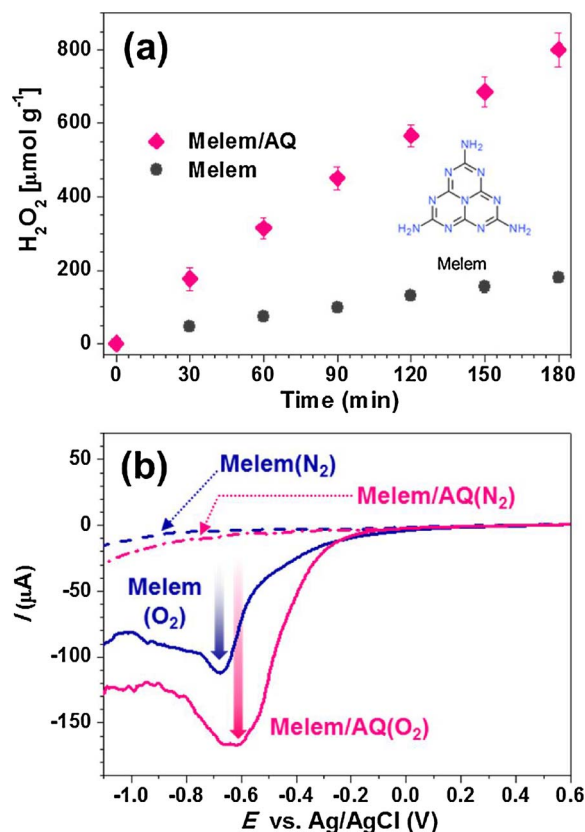


Fig. 6. (a) Time-dependent profiles of  $\text{H}_2\text{O}_2$  production by melem and melem/AQ (-COOH) (10 wt%). The experimental conditions were as follows: [catalyst] =  $0.5 \text{ g L}^{-1}$ , [2-propanol] $_0$  = 10 vol%,  $\text{pH}_i$  = not adjusted,  $100 \text{ mW cm}^{-2}$  (AM 1.5), and  $\text{O}_2$ -saturated. (b) LSV curves of melem and melem/AQ(-COOH) (10 wt%) electrodes in 0.5 M (pH = 7.0) phosphate buffer solution at a scan rate of  $50 \text{ mV s}^{-1}$  under  $\text{N}_2$ - or  $\text{O}_2$ -purging (without light).

constant (from  $0.0006 \text{ min}^{-1}$  to  $0.0003 \text{ min}^{-1}$ ). The results of PEC analyses, performed following the same procedure, led to the same conclusion: AQ functions as a co-catalyst (Figs. 6b and S13). The melem/AQ combination has a much lower  $\text{H}_2\text{O}_2$  production than  $\text{C}_3\text{N}_4/\text{AQ}$  and therefore will not be an optimal choice, but this set of data once again confirms the unique, significant role of AQ chemistry at work.

### 3.6. Quantum yields and repeated use

Fig. 7 shows the apparent quantum yield (AQY) for the  $\text{H}_2\text{O}_2$  production by  $\text{C}_3\text{N}_4$  and  $\text{C}_3\text{N}_4/\text{AQ}$  as a function of the incident monochromatic light. The AQY profile of  $\text{C}_3\text{N}_4/\text{AQ}$  closely resembles its absorption spectrum and was consistently higher than that of  $\text{C}_3\text{N}_4$ . We observed as much as an 8.3-fold enhancement under the monochromatic irradiation at 380 nm (19.5% for  $\text{C}_3\text{N}_4/\text{AQ}$  and 2.3% for  $\text{C}_3\text{N}_4$ ).

Integrating the AQY spectral response with the AM 1.5 solar spectrum yields an estimated  $\text{H}_2\text{O}_2$  production rate of  $323.1 \mu\text{mol g}^{-1} \text{h}^{-1}$  under 1-sun illumination (diameter of a circular illumination spot at ca. 2 cm), which is consistent with the  $\text{H}_2\text{O}_2$  amount quantified experimentally. The observation that the AQY profile mirrored the absorption spectrum suggests that our photocatalyst geometry has been optimized for efficient optical absorption and charge collections. However, the observation that the charge collection leading to selective  $\text{H}_2\text{O}_2$  production only reached a 20% efficiency, far from 100%, suggests the existence of additional futile recombination pathways. Further optimization of  $\text{C}_3\text{N}_4/\text{AQ}$  systems to reduce their charge or product recombination is needed.



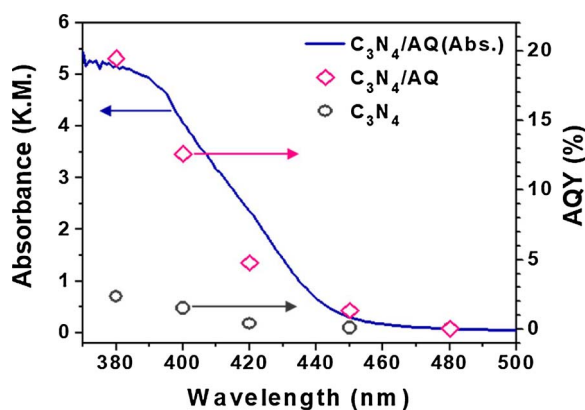


Fig. 7. (a) Absorption spectrum (left axis) and (b) apparent quantum yield (AQY, right axis) of the photocatalytic  $\text{H}_2\text{O}_2$  production as a function of wavelength on  $\text{C}_3\text{N}_4/\text{AQ}$  (10 wt%). The experimental conditions were as follows: [catalyst] =  $1 \text{ g L}^{-1}$ , [2-propanol] $_0$  = 10 vol%,  $\text{pH}_i$  = not adjusted,  $\text{O}_2$ -saturated.

#### 4. Conclusions

We have successfully demonstrated that AQ chemistry, a central mechanism that accounts for efficient and selective  $\text{H}_2\text{O}_2$  production in industrial catalytic processes, can be readily exploited to significantly enhance photocatalytic  $\text{H}_2\text{O}_2$  production when coupled with  $\text{C}_3\text{N}_4$  photocatalysts under simulated 1-sun illumination with either water or organics as an electron donor. The AQ-augmented  $\text{C}_3\text{N}_4$  (10% wt) reached an optimal  $\text{H}_2\text{O}_2$  production rate of  $361 \mu\text{mol g}^{-1} \text{ h}^{-1}$  under simulated 1-sun illumination. Compared to commonly used co-catalysts such as Ag, Au, Pt,  $\text{C}_{60}$ , and (r)GO, AQ was found to be more selective at promoting 2-electron  $\text{O}_2$  reduction to  $\text{H}_2\text{O}_2$  and suppressing decomposition of produced  $\text{H}_2\text{O}_2$ . This selectivity resulted from the unique roles of AQ as a co-catalyst that (i) effectively accepts electrons from the CB of excited  $\text{C}_3\text{N}_4$  and (ii) utilizes the electrons to initiate two-step  $\text{H}_2\text{O}_2$  synthesis (hydrogenation:  $\text{AQ} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{AQH}_2$ ; dehydrogenation:  $\text{AQH}_2 + \text{O}_2 \rightarrow \text{AQ} + \text{H}_2\text{O}_2$ ). Successful demonstration with  $\text{C}_3\text{N}_4$  suggests the possibility of other photocatalysts and photoelectrodes to achieve a similar result. For example, if a photoelectrode loaded with  $\text{C}_3\text{N}_4/\text{AQ}$  were assumed to follow the same AQY profile, we estimate that the equivalent photocurrent density would reach  $0.165 \text{ mA cm}^{-2}$ , or 0.178% solar-to-fuel conversion efficiency. Note that a water-splitting photocatalyst suspension of single-absorber  $\text{SrTiO}_3:\text{Rh}, \text{Sb}$  (Rh and Sb co-doped) particles with  $\text{IrO}_2$  co-catalysts recently showed a  $\sim 0.1\%$  solar-to-fuel conversion efficiency [64,65]. We expect that further improvement in  $\text{H}_2\text{O}_2$  production can be achieved by (i) varying the relative positions of the redox potential of  $\text{AQ}/\text{AQH}_2$  and the band edge positions of semiconductor absorbers with respect to  $\text{O}_2/\text{H}_2\text{O}_2$  potentials, (ii) anchoring AQ to photocatalysts with broader visible-light absorption spectra, and (iii) developing theoretical predictive models to optimize the absorbers/co-catalysts combination.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.01.060>.

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